

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification</b> <sup>6</sup> : <b>C02F 5/00, 5/08, 5/02</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 95/14641</b> <b>(43) International Publication Date:</b> 1 June 1995 (01.06.95)
<b>(21) International Application Number:</b> PCT/US94/13713 <b>(22) International Filing Date:</b> 28 November 1994 (28.11.94) <b>(30) Priority Data:</b> 93870228.9 29 November 1993 (29.11.93) EP <b>(34) Countries for which the regional or international application was filed:</b> AT et al. <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> BIANCHETTI, Giulia, Ottavia [IT/IT]; Viale Cesare Pavese, 410, I-00144 Roma (IT). CARDOLA, Sergio [IT/IT]; Via di Baccanello, 339, I-00064 Roma (IT). SCIALLA, Stefano [IT/IT]; Viale dei Caduti nella Guerra di Liberazione, 131, I-00128 Roma (IT). <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AU, BR, CA, FI, HU, JP, NO, US.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> LIMESCALE REMOVAL COMPOSITIONS  <b>(57) Abstract</b>  Limescale removing compositions are disclosed which comprise a C1-C6 linear or branched alkylsulfonic acid or mixtures thereof. Said alkylsulfonic acids are particularly efficient in removing limescale and they are furthermore stable to bleach/oxidants. Therefore, compositions can be formulated which further comprise acid-stable oxidant compounds. Also, mixtures of alkylsulfonic acids and sulfamic acid are particularly effective in removing limescale. The compositions of the invention are used to remove limescale from a variety of surfaces.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

## Limescale removal compositions

5

10

15

Technical Field

20 The present invention relates to compositions for the removal of limescale. The compositions herein can be used on a variety of surfaces, ranging from bathrooms and kitchen surfaces to various appliances. The compositions herein can further be used to remove limescale from dentures.

25

Background

30 Tap water always contains a certain amount of solubilized ions which eventually deposit as salts, on surfaces in contact with said water, as it evaporates. Such salts include calcium carbonate, commonly referred to as limescale. This phenomenon of limescale accumulation on surfaces which are often in contact with water may damage surfaces and affect the functioning of taps or appliances. Also, the accumulation of limescale in the toilet bowls is  
35 aesthetically unpleasant and favors the deposition of further soil and the growth of microorganisms. It is therefore important to control this limescale accumulation phenomenon.

A variety of compositions have been proposed for this purpose, which typically comprise various acids, such as hydrochloric acid. However, compositions of the art formulated with said acids require a significant amount of acid to ensure effective removal of limescale, and  
5 are thus potentially harmful to the user in case of contact with the skin, or accidental ingestion. It is thus an object of the present invention to provide limescale removing compositions which are particularly efficient in removing limescale, yet which have a lower reserve of acidity than the compositions of the art, thus which are less harmful.

10 It is also desirable to formulate compositions which comprise bleaches. Indeed, bleaches possess many desirable properties, including disinfection properties. Furthermore, such compounds as monopersulfuric acid are particularly effective as disinfectants and in removing and or decolouring stains for household cleaning applications (copending European patent application EP 93870198.4). However, bleaches in general raise compatibility issues  
15 in relation with the acids used to remove limescale. In particular, persulfuric acid is not compatible with the acids used in the art to remove limescale because persulfuric acid oxidizes the limescale removing acid upon storage, resulting in a dramatic loss of available oxygen. And by the time the product reaches the consumer, most of the available oxygen is lost. Typical acids used in the art for removing limescale, namely maleic, citric, hydrochloric  
20 and sulfamic acid are all oxidized by persulfuric acid in particular. It is thus an object of the present invention to provide a limescale removing composition which can be formulated with bleaches, in particular persulfuric acid, in a stable manner.

In response to these objects, we have now found that such a limescale removing composition  
25 could be formulated which comprises, as the acid, a C1-C6 linear or branched alkylsulfonic acid, or mixtures thereof.

#### Summary of the invention

30

The present invention thus encompasses a composition suitable for removing limescale, which comprises from 1% to 50% by weight of the total composition of a C1-C6 linear or branched alkylsulfonic acid, or mixtures thereof. In one embodiment of the invention, the  
35 compositions of the present invention preferably comprise an acid-stable bleach compound. In another embodiment of the invention, the compositions herein additionally comprise a small amount of sulfamic acid. In its broadest embodiment, the present invention further

encompasses the use of aqueous compositions comprising a C1-C6 linear or branched alkylsulfonic acid, or mixtures thereof, for removing limescale.

5

Detailed description of the invention

The compositions of the present invention are aqueous liquid compositions comprising a C1-C6 linear or branched alkylsulfonic acid, or mixtures thereof. Particularly preferred for its limescale removal performance is the use herein of methanesulfonic acid which is commercially available for example from Aldrich, William Blythe & Co. Ltd. or Elf Atochem.

10 The compositions herein comprise from 1% to 50% by weight of the total composition of said acid or mixtures thereof, preferably from 1% to 30%, most preferably 1% to 20%. The compositions according to the present invention are less harsh than the compositions of the art in that, at parity limescale removal performance, the reserve of acidity is much less than

15 the compositions in the art. Thus in this respect, in case of contact with the user's skin or in case of ingestion, the compositions of the present invention will be less harmful.

The pH of the compositions according to the present invention may range from 0 to 4, preferably 0 to 2, and is essentially determined by the type and amount of acid used.

20

In one embodiment of the present invention, the compositions herein may comprise an acid-stable bleach i.e., an oxidant compound. By acid-stable, it is meant herein a compound which is stable in the acidic environment of the compositions herein. This criterion is to be assessed on a case by case basis, depending on the specifics of given formulations. It is

25 essential that the bleach/oxidant chosen be stable at the pH of the formulation being considered. By stable, it is meant herein that the oxidant should preferably not undergo more than 30% loss of available oxygen in 6 months at room temperature (25 °C). A wide variety of oxidants have been described in the art which are suitable for use herein. Suitable acid-stable oxidant compounds for use herein include inorganic and organic peroxides. Examples

30 of inorganic peroxides are: hydrogen peroxide and sources thereof (e.g., perborate, percarbonate), persulfate salts (i.e., dipersulfate and monopersulfate salts), persulfuric acid and mixtures thereof. Examples of organic peroxides are: benzoyl peroxide, organic percarboxylic acids (i.e., peracetic acid) and mixtures thereof. Percarboxylic acids and, in general, organic or inorganic peroxides can be either solubilized in the formula or dispersed

35 in the form of suspended solids or emulsified liquids. Particularly preferred for use herein are hydrogen peroxide or sources thereof, and persulfuric acid or salts thereof because of their excellent stain removal performance and stability in acidic matrices, and mixtures thereof.

Preferred salts of persulfuric acid for use herein are monopersulfate salts, commercially available as Curox ® from Interlox. The compositions herein may comprise from 0.1% to 50% by weight of the total compositions of said acid-stable bleach/oxidant compound or mixtures thereof, preferably from 1% to 30%, most preferably 1% to 20%.

5

In another embodiment of the present invention, the compositions herein may comprise a small amount of sulfamic acid. Indeed, we have found that the combination of the alkylsulfonic acids herein together with sulfamic acid act in synergy in removing limescale. This property is particularly interesting as it allows the formulation of compositions which are particularly effective in removing limescale, while they comprise only minor amounts of sulfamic acid, thereby reducing harshness. Accordingly, the compositions herein may comprise from 0.1% to 25% by weight of the total composition of sulfamic acid, preferably from 0.1% to 20%, most preferably from 0.2% to 15%. The synergistic effect observed depends to some extent on the ratio of sulfamic acid to alkylsulfonic acid. Preferably, the ratio of sulfamic acid to alkylsulfonic acid should be of from 1:6 to 1:3. In this embodiment where sulfamic acid is incorporated in the compositions herein, it is preferred to formulate the compositions without monopersulfuric acid and similar oxidants, since monopersulfuric acid oxidizes sulfamic acid, thereby resulting in loss of available oxygen.

20 The compositions herein may further comprise surfactants since they are often used on items or surfaces which have soils or stains which do not comprise limescale, and which require the presence of surfactants in the compositions of the present invention, in order to be removed from said surfaces. Thus the compositions according to the present invention can comprise any surfactant, cationic, anionic, nonionic and zwitterionic, in amounts ranging up to 50% by weight of the total composition, preferably from 1% to 30%. Suitable anionic surfactants include alkyl or alkylene sulfates or sulfonates, alkyl or alkylene ether sulfates or sulfonates, linear alkyl benzene sulfonate and the like. Suitable cationic surfactants include quaternary ammonium salts. Suitable nonionic surfactants for use herein include ethoxylated carboxylic acids and fatty alcohol ethoxylates. For example, when the compositions herein are formulated so as to be used on inclined surfaces, it may be desirable to formulate them as emulsions of nonionic surfactants, such as in copending European patent application 9387009.1. Indeed, appropriate selection of the nonionic surfactants allows to obtain compositions with pseudoplastic profile which leads to excellent spreading and clinging characteristics.

35

The present invention can further comprise a multitude of optionals such as solvents, colorants, dyes, perfumes, stabilizers and the like.

Examples

- 5 The following compositions are made which comprise the following ingredients in the following proportions (total weight %)

Example 1

10	Dobanol @ 91-10	2.1
	Dobanol @ 91-2.5	4.9
	Methanesulfonic acid	5
	Curox @	6
	Cyclohexane	0.5
15	water and minors (e.g., dye, perfume) up to 100%	
	pH = 0.5	

Example 2

20		
	Dobanol @ 91-10	1.8
	Dobanol @ 91-2.5	4.2
	Methanesulfonic acid	10
	water and minors (e.g., dye, perfume) up to 100%	
25	pH = 0.3	

Example 3

	Dobanol @ 23-2	6
30	Dobanol @ 45-7	6
	Dobanol @ 91-10	3
	Methanesulfonic acid	5
	Hydrogen peroxide	9
	water and minors (e.g., perfume, dye) up to 100%	
35	pH = 0.5	

Example 4

	Dobanol @ 91-10	2.1
	Dobanol @ 91-2.5	4.9
5	Methanesulfonic acid	5
	water and minors (e.g., perfume, dye) up to 100%	
	pH = 0.5	

10 Example 5

	Methanesulfonic acid	5
	water and minors (e.g., perfume, dye) up to 100%	
	pH = 0.5	

15

Example 6

	Dobanol @ 91-10	1.8
20	Dobanol @ 91-2.5	4.2
	Methanesulfonic acid	5
	Curox @	3
	Hydrogen peroxide	6
	water and minors (e.g., perfume, dye) up to 100%	
25	pH = 0.5	

Example 7

30	Dobanol @ 91-10	1.8
	Dobanol @ 91-2.5	4.2
	Ethanesulfonic acid	5
	Cyclohexane	0.5
	water and minors (e.g., perfume, dye) up to 100%	
35	pH = 0.7	



Example 8

	Dobanol @ 91-10	1.8
	Dobanol @ 91-2.5	4.2
5	1-propanesulfonic acid	10
	Cyclohexane	0.5
	water and minors (e.g., perfume, dye) up to 100%	
	pH = 1	

10

Example 9

	LAS	10
	methanesulfonic acid	5
15	water and minors (e.g., perfume, dye) up to 100%	
	pH = 0.5	

Example 10

20	Dobanol @ 91-10	1.8
	Dobanol @ 91-2.5	4.2
	Methanesulfonic acid	7.5
	Sulfamic acid	2.5
	water and minors (e.g., perfume, dye) up to 100%	
25	pH = 0.3	

Example 11

	Dobanol @ 91-10	1.8
30	Dobanol @ 91-2.5	4.2
	Methanesulfonic acid	9
	Sulfamic acid	1
	water and minors (e.g., perfume, dye) up to 100%	
	pH = 0.2	

35

Example 12

	Dobanol @ 91-10	1.8
	Dobanol @ 91-2.5	4.2
5	Methanesulfonic acid	5
	Sulfamic acid	5
	water and minors (e.g., perfume, dye) up to 100%	
	pH = 0.4	

- 10 The limescale removal efficiency of samples is evaluated by putting a block of 6 g of calcium carbonate in 50 mls of the sample to be evaluated for a period of 30 minutes. The block is weighed dry before and after the experiment. We have measured that with composition 4, the weight decrease was 0.83g and 1.1g for composition 5. In the same composition, where methanesulfonic acid is replaced by the same weight quantity of sulfamic acid, the weight
- 15 decrease is only 0.731g. We have also measured that it takes 13% of hydrochloric acid in a product marketed under the trade name of WC Net® to obtain a similar result (weight decrease 0.84g) as with 5% methanesulfonic acid. Also, composition 10 illustrates that mixtures of alkylsulfonic acids with sulfamic acids are particularly effective in removing limescale. In the same experiment, we measured a weight decrease of 1.06g with
- 20 composition 10, while the same composition but with 10% methanesulfonic acid (composition 2) only, instead, gave 0.87g decrease, and the same composition but with 10% sulfamic acid only, instead, gave 0.85g decrease. Thus when combining the alkylsulfonic acids of the present invention with sulfamic acid, a better performance is obtained with a the same total amount of acid than with either of these acids alone. The synergistic effect of mixtures of
- 25 sulfamic acid with alkylsulfonic acid, in this case methanesulfonic acid, is maximized at certain ratios. Composition 11 and 12, outside the preferred ratio range, give a weight decrease of respectively 0.90g and 0.93g. This performance is better than the performance obtained with either acids alone but poorer than the performance obtained with composition 10 comprising a mixture of both acids within the preferred ratio range.
- 30 In terms of reserve of acidity, we have measured that it takes 1.88g NaOH/100g product to bring composition 1 to pH4, while it takes 16.8g NaOH/100g product to bring to pH 4 a composition marketed under the trade name WC Net ®. Similarly, it takes 15.5g NaOH/100g product to bring to pH 4 a composition marketed under the trade name Harpic
- 35 limescale Remover ®. Thus composition 1 has much less reserve of acidity and is therefore less harmful to the user.

In terms of bleach stability, the available oxygen is monitored in composition 1. The available oxygen is measured in the fresh composition, and in the same composition after one week storage at room temperature (25 °C). We have measured there was no loss of available oxygen with composition 1 whereas in the same compositions where  
5 methanesulfonic acid was replaced respectively by the same amount (weight) of sulfamic or hydrochloric acid, the loss of available oxygen in the same period ranges between 66% and 98%. Thus the compositions according to the present invention are much more stable

What is Claimed is:

1. The use of an aqueous composition comprising a C1-C6 linear or branched alkylsulfonic acid, or mixtures thereof, for removing limescale.
2. The use of a C1-C6 linear or branched alkylsulfonic acid, or mixtures thereof, for the manufacture of an aqueous composition for removing limescale.
3. A composition suitable for removing limescale, which comprises an acid, characterized in that said acid comprises from 1% to 50% by weight of the total composition of a C1-C6 linear or branched alkylsulfonic acid, or mixtures thereof.
4. A composition or use according to the preceding claims wherein said composition further comprises an acid-stable oxidant compound, or mixtures thereof.
5. A composition or use according to claim 4 wherein said oxidant is hydrogen peroxide or a salt of persulfuric acid, preferably a monopersulfate salt.
6. A composition or use according to the preceding claims which further comprises up to 50% by weight of the total composition of a surfactant system.
7. A composition or use according to claims 1-4 and 6 which further comprises sulfamic acid, preferably in amount of from 0.1% to 25% by weight of the total composition, preferably from 0.1% to 20%, most preferably from 0.2% to 15%.
8. A composition or use according to claim 7 wherein the ratio of sulfamic acid to alkylsulfonic acid is from 1:3 to 1:6.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/13713

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :C02F 5/00, 5/08, 5/02

US CL : 252/80, 82, 180; 210/700, 699

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/80, 82, 180; 210/699, 700

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 4,581,161 (Nedonchelle) 08 April 1986	1-8
A	US,A, 4,759,867 (Choy et al) 26 July 1988	1-8
A	US,A, 4,895,669 (Choy et al) 23 January 1990	1-8
A	US,A, 5,039,441 (Thomas et al) 13 August 1991	1-8

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

14 FEBRUARY 1995

Date of mailing of the international search report

13 MAR 1995

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

PRINCE E. WILLIS, JR

Telephone No. (703) 308-3050

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/13713

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 5,087,376 (Bendiksen et al) 11 February 1992	1-8
A	US,A, 5,254,290 (Blandiaux et al) 19 October 1993.	1-8